A COMBUSTION BOMB METHOD FOR THE DETERMINATION OF MERCURY IN COAL

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INTRODUCTION

Earlier workers have described the use of an oxygen combustion bomb in conjunction with procedures for determining trace amounts of mercury in a variety of organic substances. In 1958, Borchardt and Browning reported a procedure for the analysis of microgram quantities of mercury in paper. (1) One-gram samples of paper were rolled into a cylinder, placed inside a platinum coil, and ignited under 25 to 30 atm of oxygen in a Parr combustion bomb containing 15 ml of 0.1 N potassium permanganate solution and 10 ml of 10 percent sulfuric acid solution. The contents of the bomb were subsequently transferred to a separatory funnel, treated with hydroxylamine sulfate solution to reduce the permanganate, and extracted with a dithizone solution in chloroform. Mercury was determined colorimetrically on the dithizone-chloroform extract. The method was found to be suitable for the determination of mercury in the range of 1 to 10 micrograms per gram (ppm).

Various modifications of the procedure of Borchardt and Browning have been reported by several workers at the University of Tokyo. Thus, Fujita et al. described a similar technique in which combustion was carried out in the presence of 1.0 N nitric acid previously added to the bomb. (2) The oxidation products were subsequently reduced by the addition of hydroxylamine hydrochloride and urea solutions, and mercury was extracted with a solution of dithizone in carbon tetrachloride. The procedure was developed primarily for the determination of mercury in rice which had been treated with mercurial fungicides, although various other materials including vegetable oils, human hair, and tissue samples from mercury-poisoned rats were analyzed with apparent success. Values as low as 0.17 ppm were reported for the combustion of 4 grams of unpolished rice grain (the maximum amount that could be burned completely in the bomb).

Fujiwara and Narasaki have discussed the relative merits of using the oxygen combustion bomb for trace element determinations in a variety of samples. (3) They suggested that the interior of the bomb should be platinum-coated to reduce contamination of the sample or interactions of the combustion products with the bomb walls.

Ukita et al. also reported the determination of mercury in rice, wheat, and various biological materials by a combination of the bomb combustion method and atomic absorption spectrophotometry. (4) The combustion procedure was similar to that of Borchardt and Browning in that a potassium permanganate solution, acidified with sulfuric acid, was used in the bomb to trap combustion products. After combustion, the liquid from the bomb was

treated with hydroxylamine hydrochloride, rinsed into a 100 ml volumetric flask, and diluted with 1 N sulfuric acid. Aliquots of this solution were treated with 10 percent stannous chloride solution to reduce mercury, which was then determined by a flameless atomic absorption technique. Ukita et al. advocate the use of a platinum-coated stainless steel bomb to avoid dissolution of trace amounts of iron, nickel, and other metals from the bomb walls during combustion. However, it was also reported that these extraneous metals did not interfere with the determination of mercury by the stannous chloride reduction method. Detection limits as low as 0.05 µg for samples of 0.5 to 1.0 g were reported.

This paper describes a procedure for the determination of nanogram quantities of mercury in whole coal. The method involves decomposition of the coal in a combustion bomb under 24 atm of oxygen in the presence of a nitric acid solution containing hydroxylamine hydrochloride. Following combustion, the contents of the bomb are diluted to a known volume and mercury is determined by a flameless atomic absorption technique involving stannous chloride reduction. The procedure has given repeatable results for the analysis of trace amounts of mercury in coal, and it can be carried out with standard equipment accessible to most coal analysis laboratories.

<div align="center">EXPERIMENTAL</div>

Apparatus

Combustions were carried out in a standard 360 ml stainless steel combustion bomb (Parr Instrument Co., Model No. 1102) using No. 34 B. & S. gauge nichrome fuse wire and a quartz combustion crucible. The crucible, originally of 10 ml capacity, had to be cut down with a diamond saw to about 6 ml capacity to allow proper placement of the fuse wire in the bomb. Other components of the Parr Series 1200 adiabatic calorimeter, including the Series 2900 ignition unit, were used routinely in these tests.

An Instrumentation Laboratory Model 153 atomic absorption spectrophotometer, incorporating a Varian Techtron hollow cathode mercury lamp and a 100 millivolt Honeywell Electronik 194 strip chart recorder, was used for the spectrophotometric determination of mercury. The instrument conditions were maintained as follows: slit width, 320 µm; wavelength, 253.7 nm; scale, 0.25; photomultiplier tube (R 372) voltage, 620 v; hollow cathode lamp current, 4 ma; mode, high damp; gas flow, 1 liter He/min; chart speed, 1 inch/min. The absorption cell, shown in Figure 1, consisted of a Plexiglas tube 125 mm long and 22 mm I.D.; the tube was fitted with removable quartz windows by means of modified polyethylene snap caps. The cell was mounted directly on top of the nitrous oxide burner head, and its position could be adjusted using the standard controls on the instrument. A cylindrical, flat-bottom cold test jar (Fisher No. 13-415) of approximately 100 ml capacity and incorporating a Teflon-covered micro stirring bar was employed as the reaction vessel for stannous chloride reductions. Helium purge gas was admitted to the reaction vessel through a fritted gas dispersion tube. Connections to the absorption cell were made with Tygon tubing.
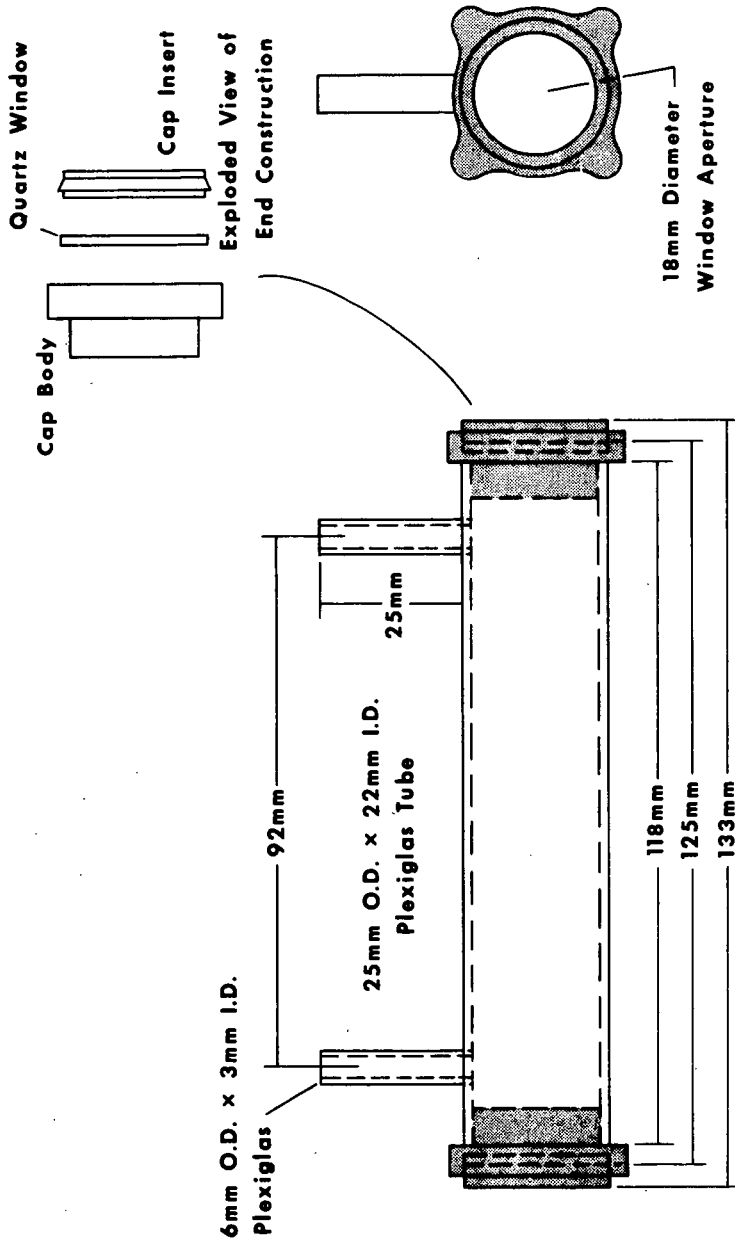
Quartz Window

Cap Insert

Cap Body

Exploded View of
End Construction

18mm Diameter
Window Aperture

6mm O.D. × 3mm I.D.
Plexiglas

25mm O.D. × 22mm I.D.
Plexiglas Tube

92mm

25mm

118mm
125mm
133mm

Figure 1. Mercury Absorption Cell

Procedure

A 0.500 gram sample of minus 60 mesh coal was weighed in a tared quartz combustion crucible. The crucible was placed in the electrode support of a stainless steel bomb containing 20 ml each of 1 N nitric acid and 10 percent hydroxylamine hydrochloride solution. The level of the liquid in the bomb should be below the bottom of the combustion crucible to avoid incomplete combustions. The fuse wire was attached, the bomb was assembled, and oxygen gas was added to a pressure of 24 atm (gauge). The bomb was then placed in the calorimeter (a cold water bath in a large stainless steel beaker is also satisfactory) and the sample was ignited using appropriate safety precautions ordinarily employed in bomb calorimetry work. After combustion and a temperature equilibration period of about five minutes, the bomb was rolled on its side several times to rinse down the inner walls and the combustion gases were slowly released. The bomb was then opened and its contents were emptied into a 100 ml volumetric flask. The interior surfaces of the bomb and the quartz crucible were rinsed well with 1 N nitric acid and the volumetric flask was filled to the mark with 1 N nitric acid.

Ordinarily, a 10 ml aliquot of the sample solution was pipetted into the reaction vessel containing the micro magnetic stirring bar. However, the size of the aliquot could be varied between 1 and 15 ml depending on the mercury concentration. Approximately 2 ml of a 1 percent stannous chloride solution was added using a Pasteur pipet, and the sample was diluted to a total volume of 20 ml with deionized water. The reaction vessel was then stoppered and the helium inlet tube was adjusted so that the frit was just above the stirring bar. The solution was stirred for one minute, after which the helium purge gas flow was initiated at a rate of one liter per minute. The gas was not recirculated as in some procedures, but was passed directly through the absorption cell and into an exhaust system. The absorption peak height was recorded on the strip chart and was converted to nanograms of mercury by comparison with standards run under the same conditions. All results were corrected for reagent blanks.

RESULTS AND DISCUSSION

A sample of Lower Kittanning seam coal was analyzed by the procedure described above. Results from 21 separate combustion tests over a 6-month period were used in evaluating the precision of the method. In each test, duplicate 10-ml aliquots of the sample solution were taken for atomic absorption analysis. These data showed a mean mercury concentration of 0.319 µg per gram of coal (as-received basis) with a standard deviation of 0.015 µg, corresponding to a relative standard deviation of 4.8 percent.

This same coal has also been analyzed for mercury elsewhere by other techniques, including neutron activation and the dithizone colorimetric method. Based on a statistical analysis of these independent results, the calculated "best value" for the Lower Kittanning coal has been reported as 0.31 ± 0.03 µg/g. (5) This result is considered to be in good agreement with that obtained by the oxygen combustion bomb method.

Mercury present in the 10 ml aliquot taken after the combustion of
0.500 g of the Lower Kittanning coal generally produced a peak height of
about 20 chart divisions on the strip chart recorder. After subtraction of
the reagent blank, which was normally about 4 chart divisions, the re-
mainder of 16 chart divisions corresponded to the 16 ng of mercury actually
present in the 10 ml aliquot. The most widely used definition of detection
limit is that concentration of an element necessary to displace the average
absorbance reading by an amount equivalent to the peak-to-peak noise of the
base line. (6) At the instrument settings employed in these measurements,
the background noise was ordinarily $\pm$ 1 chart division. Thus, the detection
limit of the method was on the order of 0.040 µg/g. This detection limit
can be improved, of course, by the use of larger coal samples for combustion
(up to 1.0 g) and/or larger aliquots of the solution taken for stannous
chloride reduction.

It was found necessary to check for background levels of mercury in the
combustion bomb at frequent intervals, particularly after a comparatively
large amount of mercury had been introduced to the bomb via unknowns or
standards. This was accomplished by repeated firings of 0.5 g benzoic acid
pellets until a stable, consistently low blank was obtained. In addition,
the condition of the bomb itself is believed to be quite critical to the
success of the procedure. Thus, at one point in the development of the
method, it was observed that mercury recoveries from both standards and pre-
viously analyzed coal samples were unexplainably low. An inspection of the
bomb revealed numerous small cracks and fissures on the inner walls of the
bomb. The bomb was sent to the manufacturer for reboring, polishing, and
pressure testing, and after it was returned normal results were once again
obtained.

The presence of chloride ion in the trapping solution is apparently
necessary to stabilize the mercury released from the coal during combustion,
presumably through the formation of complex ions. In the absence of a
chloride ion source, the results were erratic and mercury recoveries were
usually low. In addition to hydroxylamine hydrochloride, both ammonium
chloride and sodium chloride were used with comparable results, although the
latter has the disadvantage of introducing extraneous metal cations to the
system. Hydrochloric acid would probably be the preferred reagent for this
purpose, although all samples of reagent grade HCl employed in these studies
were found to contain significant trace levels of mercury, leading to un-
acceptably high reagent blanks.

The effects of several variables involved in the cold vapor atomic
absorption step of the procedure were investigated. The first of these was
the flow rate of helium gas used to entrain the mercury vapor subsequent to
stannous chloride reduction. The results of these tests for standard
solutions containing 100 ng of mercury are shown in Table 1. The data indi-
cate that sensitivity can be increased by decreasing the helium flow rate.
However, above 1.0 liter/min the increases are marginal and are offset by
impractically long peak recording times. For these reasons, a flow rate of
1.0 liter/min was considered to be the optimum setting.

TABLE 1. EFFECT OF HELIUM FLOW RATE ON PEAK
HEIGHT AND PEAK RECORDING TIME.

Flow Rate, liters/min	Peak Height, chart divisions	Peak Recording time, min
3.5	31.0	0.50
2.5	33.4	0.50
1.6	41.5	0.50
1.0	48.3	0.75
0.4	52.5	2.00
0.1	54.5	6.00

A second variable involves the unoccupied or dead space volume above
the solution in the reaction vessel, which is dependent on the volume of
the reaction vessel as well as the volume of solution contained therein.
Although the results of these tests were not sufficiently consistent to
afford a good correlation, there was a definite indication that the sen-
sitivity was increased as the dead space volume decreased. This relation-
ship was particularly evident as the size of the reaction vessel was de-
creased. The results suggested that the reaction vessel should be as
small as possible, yet sufficiently large to avoid carry-over of appre-
ciable amounts of moisture into the absorption cell due to frothing of the
sample (this problem was observed frequently during the course of these
studies).

A third variable considered was the reaction time (with stirring) be-
tween the addition of the reducing agent and the beginning of the helium
gas purge. The results with standard solutions containing 100 ng of mercury
were essentially identical over a range of reaction times between 10 seconds
and 4 minutes. Consequently, a reaction period of one minute was judged to
be adequate for the procedure.

The combustion bomb method for the determination of mercury in coal has
given reproducible results for several coals analyzed in this laboratory.
However, there are several parameters involved in the overall procedure which
have not been quantified, and further work would be helpful in defining their
effects. These include the following:

1. Both the concentrations and volumes of the nitric acid and hydroxy-
lamine hydrochloride solutions used in the bomb to trap mercury.

2. The length of time the solution remains in the bomb after firing
the sample. Preliminary data have indicated that waiting periods on the
order of one hour resulted in significant losses of mercury.

3. Handling of the bomb after combustion. Although some amount of mixing of the contents would seem desirable, vigorous agitation is precluded by the presence of the silica combustion capsule in the bomb, as well as the possibility that some of the liquid will enter the valve mechanism and be subsequently expelled when pressure is released from the bomb.

4. Loss of mercury due to adsorption on the walls of the bomb. Although this effect is known to exist, it seems to occur in an erratic fashion and can only be compensated for by firing blanks of benzoic acid until a stable background level of mercury is obtained. This effect is particularly troublesome, as the mercury adsorbed during combustion of one sample may be later desorbed to contaminate a subsequent sample.

5. The timing of various steps in the procedure involving transfer and dilution of the sample solution prior to atomic absorption analysis. Each of these operations involves possible loss of or contamination from adsorbed mercury. Although attempts were generally made in these studies to carry out the atomic absorption analysis as soon as possible after combusting the sample, the chronology of operations in this phase of the procedure was not entirely consistent.

In summary, the oxygen combustion bomb procedure as described herein is considered reliable for the analysis of trace amounts of mercury in coal. It is sufficiently simple and rapid, and can be carried out with equipment available in most modern coal analysis laboratories.

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